A New Group-Contribution Lattice Fluid Equation of State with Hydrogen bonding and Dimerization Consideration

Jeong Won Kang, Ki-Pung Yoo[#], Chul Soo Lee*

Dep. of Chemical and Biological Engineering, Korea University, Seoul 136-701, Korea
[#]Dept. of Chemical Engineering, Sogang University Seoul 121-742, Korea
*To whom the correspondence should be addressed. cslee@korea.ac.kr

Abstracts

Equations of state provide thermodynamic properties and phase equilibria over a wide range of pressure. Group contribution methods applied to equations of state are convenient for properties predictions as well as calculations. Yet, they are still in the developing stage. Methods have been proposed for physical interactions so far, which are not very accurate for mixtures with associating components. Lattice fluid models have been a convenient basis for group contribution methods is now developed to include associating interactions. In the present study the hydrogen-bonding non-random lattice fluid model was put to group contribution forms and applied to alkanes, aromatics, alcohols and their mixtures. Error in vapor pressure and density for pure components was about 1 % and those for bubble pressure and vapor composition was about 2 % in most cases.

Introduction

Group contribution excess Gibbs function models such as UNIFAC and ASOG have long been in use. However, group contribution equations of state (GC-EOS) are still in developing stages. Equation of state approach provides information on residual properties of real fluids and, thus, is applicable to various properties such as volume, enthalpy and phase equilibria in principle. In particular, an equation of state is needed for high-pressure properties, for which the use of an excess Gibbs function model is generally not adequate.

Lattice based statistics have been a convenient basis of GC-EOS approaches [1-5] as well as of group contribution excess Gibbs function approaches. Danner and coworkers obtained molecular segment number from corresponding group parameters, but molecular surface area parameters and corresponding group parameters were not related [2, 4]. They defined *ij* group interaction energy as a geometric mean of *ii* and *jj* pairs. In

some studies [3, 5] group surface area parameters were set equal to group segment numbers. In these methods group segment numbers add up to give molecular segment number but group surface area parameters do not add up to corresponding molecular surface area parameters in most approaches. Victorov and Smirnova's group version lattice fluid formulation avoids the problem of the surface area parameters [1]. However, in their formulation the molecular segment number is irrelevant and the group bulkiness parameter was used as a fitting parameter.

All these approaches were for physical interactions and association contributions were not included. Without association contributions, previous GC-EOS studies lead to excessive errors for phase equilibira of mixtures containing associating components [1, 3, 5]. Also problems with segment numbers or surface area parameters need to be solved.

In a non-group contribution version of lattice fluid equations of state developed by present authors based on the Guggenheim combinatory, the implicit nonrandom physical contribution was made explicit by an expansion method [6,7] and the association contribution due to Veytsmann was revised and extended to include dimer formation [8]. When compared with data and other models, the resulting hydrogen-bonding nonrandom lattice fluid model (NLF-HB) was found to provide an accurate description of fluid properties [9], making the model a sound basis for a GC-EOS approach.

As will be explained, association contributions are in a form suitable for group contribution formulations. Park et al. [5] suggested a means of resolving the incompatibility of surface area parameters. These considerations are the basis for the new GC-EOS approach that is presented in the present paper.

GC-EOS model and Parameters

The configurational Helmholtz free energy of a mixture of N_1, N_2, …., and N_C molecules of components 1, 2, …., and C is represented by a sum of physical and association contributions.

$$A^C = A_{phys} + A_{ass} \tag{1}$$

The physical contribution is characterized by molecular segment number, r_i, and the mean energy of interactions between segments, ε_{ij}. The surface area parameter, q_i, is related to segment number by,

$$zq_i = r_i(z-2) + 2 \tag{2}$$

where z is the coordination number. In addition the unit lattice cell volume V_H is needed. There are also N_0 holes in the mixture with r_0=1 and ε_{0i}=ε_{i0}=0. Expressions for the Helmholtz free energy are given in the reference [6].

To evaluate the association contribution, the number of donor type k, d_k^i, that of acceptor type l, a_l^i, in species i, and the association free energy between donor type k and accptor type l, A_{kl}^H, are required.

$$A_{kl}^H = U_{kl}^H - TS_{kl}^H \tag{3}$$

where U_{kl}^H and S_{kl}^H are energy and entropy of association. In addition the active segement number of a donor or an acceptor, r_H, is needed, which is independent of species. Expressions for the association contribution are given in the reference [8].

Association contribution is in the group contribution formalism and no further formulation is needed for group contribution applications. The molecular physical interaction parameters need to be obtained from corresponding group parameters.

$$r_i = \sum \nu_i^q r_q^G \tag{4}$$

$$\varepsilon_{ij} = \sum \sum \theta_i^q \theta_j^r \varepsilon_{qr}^G \tag{5}$$

where ν_i^q is the number of type q groups in component i and

$$\theta_i^q = \nu_i^q q_q^G / \sum_m \nu_i^m q_m^G \tag{6}$$

The group surface area parameter is related to the group segment number by

$$zq_q^G = r_q^G (z-2) + 2(1 - l_q^G) \tag{7}$$

where l_q^G is the group bulkiness parameter or more rightly the group connectivity parameter. $2l_q^G$ represents the number of contacts to adjacent groups. Thus l_q^G equals 0.5 for a singly connected group, 1 for a doubly connected group, etc. In this way group surface area parameters and group segment numbers are correctly added to give corresponding parameters and numbers for molecules [5].

We have group parameters r_q^G, ε_{qr}^G, U_{kl}^H, S_{kl}^H for fitted group variables, l_q^G for group connectivity constants, d_k^i and a_l^i for species dependent constants, and z, V_H and r_H for universal lattice constants. As in previous studies universal constants are set to 10, 9.75 cm^3/mol and 0.05 for z, V_H, and r_H, respectively. l_q^G value is self evident as explained above. d_k^i and a_l^i values are clearly known in most cases, 1 and 1 for alcohols, for example. Values for U_{kl}^H and S_{kl}^H are known in the literature for some donor-acceptor pairs. As in our previous studies [3, 5-9] both segment numbers and energy

parameters were made temperature dependent for more accurate fitting. The temperature dependences of the segment number and the energy parameter are represented by

$$r_i = r_a^G + r_b^G (T - T_0) + r_c^G (T \ln T_0 / T + T - T_0) \quad (8)$$

$$\varepsilon_{ij} / k = (\varepsilon_a^G / k) + (\varepsilon_b^G / k)(T - T_0) + (\varepsilon_c^G / k)(T \ln T_0 / T + T - T_0) \quad (9)$$

where T_0=298.15 K.

Results and Discussions

The present formulation of the GC-EOS based on the Guggenheim combinatory is most general in the sense that both nonrandom and association contributions are included in the model. Association contributions were not included in previous GC-EOS studies. Danner and coworkers did not include nonrandom contributions. In previous studies of present authors the inconsistency of surface area parameters in the group and molecular levels were present. Victorov and Smirnova works were for segment species rather then molecular species.

For the determination of physical parameters, we began with alkanes from C4 to C10. Segment numbers and interaction energy parameters were fitted to isothermal vapor pressures and densities of pure component at several temperatures in the temperature range of 300-400 K. Then the segment numbers were regressed to group parameters and listed in Table 1. For light molecules such as methane, ethane and propane were not decomposed into groups and their parameters were fitted to isothermal pressure-volume data.

Group-group interaction energy parameters were fitted to data for vapor liquid equilbria and vapor pressure at several temperatures in the same temperature range using the segment number values in Table 1 and regressed to obtain temperature coefficients given in Table 2. Fitting errors for densities and vapor pressures are listed in Table 3 and those for vapor liquid equilibria are shown in Table 4. Similar procedures apply to the determination of physical parameters of associating groups using hydrogen-bonding parameters for the non-group version of the present EOS, U_{kl}^H= –26.5 kJ/mol and S_{kl}^H= -26.5 J/K·mol. Regressed parameters are also listed in Tables 1 and 2. For interactions with methane the regression was done at one temperature and the values at the temperature are shown in the table. Fitting errors were given in Tables 3 and 4. The errors in vapor pressure and density turn out to be slightly inferior to the results of non-group version of the present approach [9] for wider ranges of temperatures.

Results of equlibirum pressure calculations are compared with those of the non-group version in Table 5. Again the results of the present group version are only slightly inferior. Comprehensive comparisons with previous non-associating models for non-polar and associating mixtures are yet to be made. Fig. 1 shows high-pressure phase equilibria for metane+decane system. As an example of phase equilibria involving associating component, heptane+butanol system is shown in Fig. 2. Both figures show that the present group contribution method is satisfactory for high pressure or associating systems.

Conclusions

Based on the hydrogen-bonding non-random lattice fluid model by present authors a group contribution equation of state method was developed. The method was applied to alkanes, aromatics, alcohols and their mixtures and was found accurate for non-associating and associating components and their mixtures up to high pressures. Error in vapor pressure and density for pure components was about 1 % and those for bubble pressure and vapor composition was about 2 % in most cases.

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Table 1. Group Segment Numbers

Group	$r^G{}_a$	$r^G{}_b$	$r^G{}_c$	l_i
CH3	2.6293	-3.5423E-4	3.0078E-3	0.5
CH2	1.5525	-7.0335E-5	6.0318E-4	1.0
ACH	1.4008	1.7078E-4	9.7940E-4	1.0
ACCH3	2.9927	-8.5680E-4	-5.9319E-4	1.0
CH2OH	2.5101	9.6975E-4	-2.2452E-3	0.5
CH4	4.562587	9.0461E-3	-0.0154	0.0

Table.2 Energy Parameters for Group-Group Interactions

Group	$\varepsilon^{G}{}_{a}$	$\varepsilon^{G}{}_{b}$	$\varepsilon^{G}{}_{c}$	T range
CH3 + CH3	79.8206	0.0152	-0.0762	250 – 500 K
CH3 + CH2	93.9827	0.0159	-0.0168	250 – 500 K
CH2 + CH2	115.7860	0.0546	0.0101	250 – 500 K
CH3 + CH2OH	97.1803	2.2846E-4	0.2171	260 – 400 K
CH2 + CH2OH	117.1820	4.7304E-3	-0.1136	260 – 400 K
CH2OH + CH2OH	138.0330	0.0158	-0.2197	260 – 400 K
ACH + ACH	119.8611	-8.5475E-3	-0.0854	300 – 400 K
ACH + CH3	96.3214	0.0162	0.4326	300 – 400 K
ACH + CH2	114.3613	0.0334	-0.3465	300 – 400 K
ACCH3 + ACCH3	116.0315	0.0666	0.1706	300 – 400 K
ACCH3 + ACH	116.7830	0.0235	-0.0485	300 – 400 K
ACCH3 + CH3	92.2029	-0.1962	-1.3486	300 – 400 K
ACCH3 + CH2	119.2289	0.2093	1.4554	300 – 400 K
ACH + CH2OH	124.0354	0.0496	0.2279	278 – 348 K
ACCH3 + CH2OH	125.4984	-0.1983	-2.1642	300 – 400 K
CH4 + CH4	48.6604			344.26 K
CH4 + CH3	63.2106			344.26 K
CH4 + CH2	84.2387			344.26 K

Table.3 Fitting Errors for Densities and Vapor Pressures

Component Type	ΔP (%)	$\Delta\rho$ (%)	T Range
n-Alkane	1.30	0.25	250 – 500 K
1-Alkanol	1.08	1.65	260 – 400 K
Aromatics	1.02	0.80	300 – 400 K

Table.4 Fitting Errors for Vapor-Liquid Equilibria

Mixture Type	ΔP (%)	Data Points	Δy (%)	Data Points	T Range (K)
Non Associating Mixtures					
n-Alkane + n-Alkane	1.97	435	1.86	94	250-500
n-Alkane + Benzene	2.02	761	1.06	363	300-400
n-Alkane + Toluene, Xylene	2.46	375	2.93	258	300-400
Benzene + Toluene, Xylene	0.75	117	1.30	101	300-400
Associating Mixtures					
n-Alkane + 1-Alkanol	2.30	652	1.50	376	260-400
Benzene + 1-Alcohol	2.51	300	3.98	163	273-350
Toluene, Xylene + 1-Alcohol	3.78	326	4.04	318	300-400

Table.5 Comparison of VLE errors for molecular version EOS and group version EOS.

Mixture Type	ΔP (%) Molecular Version EOS	ΔP (%) Group Version EOS
n-Alkane + n-Alkane	0.55	1.97
n-Alkane + 1-Alkanol	1.37	2.30

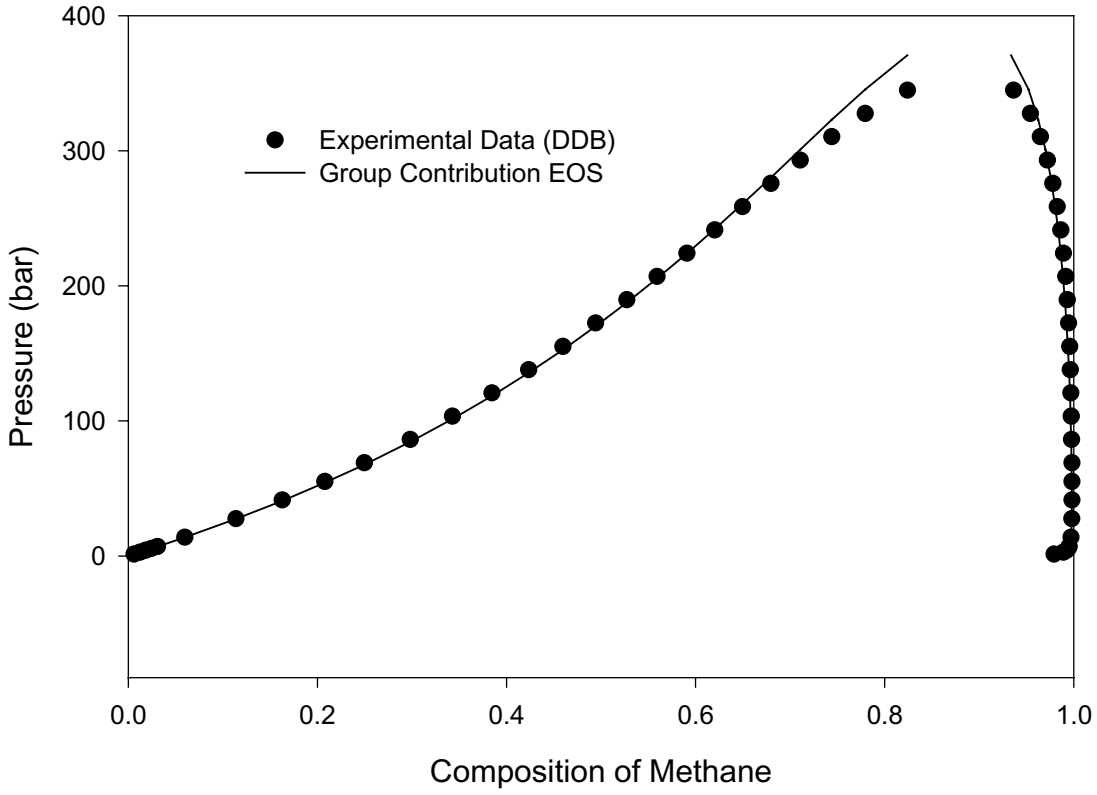

Figure 1. Comparision of Experimental data with calculation result for methane + decane system at 344.26K

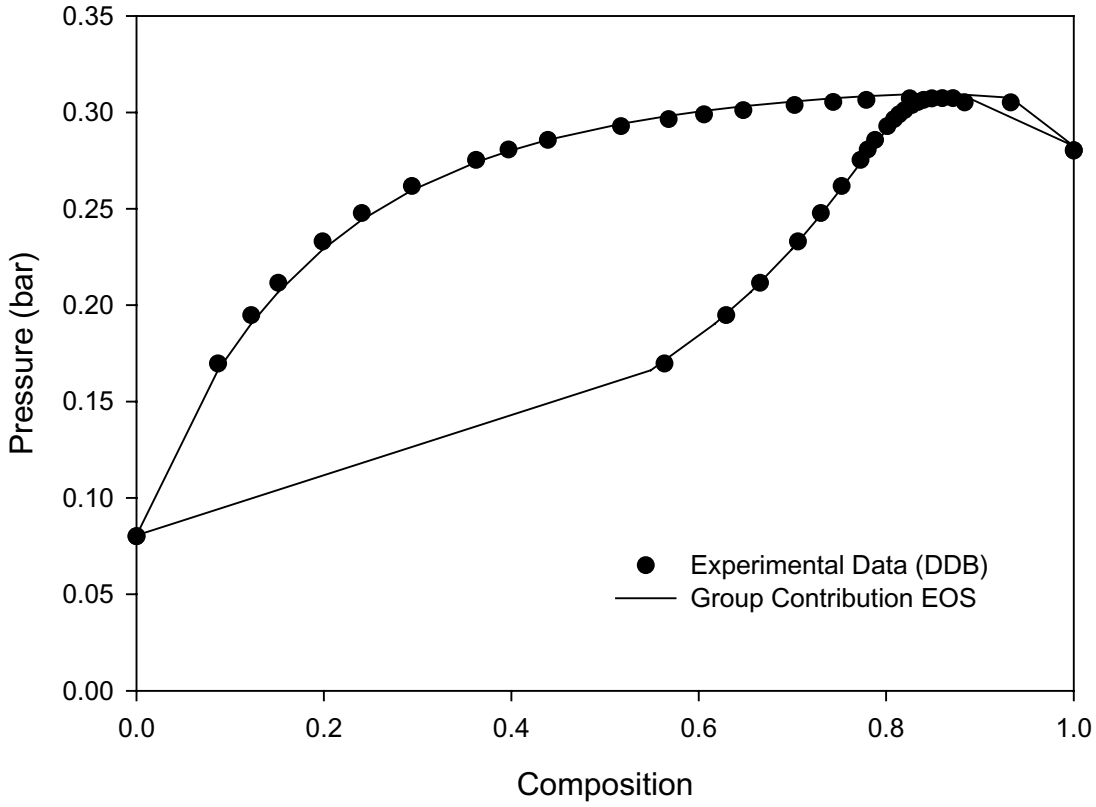

Figure 2. Comparison of Experimental Data with Calculation Result for Hepatne + 1-Butanol at 333.15 K